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FINAL REPORT ON EVALUATION OF

CANMET NASICON CERAMICS IN SODIUM/SODIUM CELLS

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I INTRODUCTION

Nine samples of Nasicon discs were forwarded to the Ceramic Engineering Research Group at McMaster University by Dr. A.K. Kuriakose for the testing in sodium-sodium cells. They had been prepared by different routes using variable conditions of time and sintering temperature (Table I). The initial characterisation was the electrical testing using the a.c. impedance technique and then in sodium environments to evaluate the degradation of each electrolyte. The discs as received were tested as described below.

II EXPERIMENTAL

Before assembling the discs in Na/Na cells, their a.c. impedance was measured.

The first requirement was to prepare the surfaces of each disc and this was done via three steps (a) by grinding to a parallel surface on a diamond wheel; (b) grinding on a rotating wheel using a #600 grade wet emery paper (methanol being used); (c) mechanically polishing using diamond paste down to 1 μm. The final mean thicknesses and diameters of the discs were recorded (Table II).

X-ray diffraction was carried out on randomly selected discs and it showed the materials to be crystalline.

The sample designated GEL-MP 2.0)#19, 1175^{o}C - 16 hrs, had a density of 3.07 gcm^{-3} and was tested ultrasonically. This was carried out by the NDE

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ABSTRACT

Nous avons effectué des cycles galvanostatiques sur des cellules sodium/sodium utilisant des ceramiques Nasicon de differentes compositions comme electrolyte. Les courbes caracteristiques tension-temps de ces cellules et l'état des ceramiques après les cycles indiquent que ces ceramiques Nasicon ne sont pas assez durables pour être utilisées en tant qu'electrolytes solides.

group. The scans were performed with the transducer (75MHz) just above the sample. Neither the transducer nor the sample were levelled. The transducer was tilted to provide a minimum signal from both the top and bottom of the sample. The sample was scanned in silicon oil (Edwards Diffusion Pump Oil). It was taped to the bottom of the petri-dish using double sided tape.

The initial and final positions were found by moving the sample until the signal from the transducer disappeared. Several photographs were taken at various points and in each case, the receiver was set to zero decibel attenuation, 500Ω damping. During the scanning of the sample, no single signal stood out, indicative of a definite defect. However, the signals changed continuously. This change was small, almost like ripples. Certain regions had definite patterns, but whether this was due to defects or surfaces is uncertain. A typical ultrasonic spectrum is shown in Figure 1, indicating the forward and backward reflection and the scan through the sample. Further ultrasonic measurements on other discs were abandoned due to the wide range of pits and cracks on the surface of those samples that would otherwise have led to uncertain results.

The a.c. impedance of each Nasicon disc was measured as a function of temperature. The impedance circuit used in our work is shown in Figure 2. The data were collated and logged into a computer from which the D.C. resistance and activation energy for sodium ion conduction were obtained. The technique utilised a non-blocking $Pt/NaNO_2/NaNO_3//$nasicon electrolyte$//NaNO_3/NaNO_2/Pt$ system. The frequency range studied was that between 50 Hz and 12 kHz. In some cases, higher frequencies than 12 kHz were employed but without further effect on the results.

Once the electrical impedance had been measured, the electrolytes were characterised in sodium-sodium cells.

The essential features of the cell used in our work are shown in Figure 3. The cell was made of stainless steel to avoid corrosion problems. High-temperature-resistant graphite gaskets were used to prevent air entering the system. Current collection from one of the electrode was made via a glass-metal seal using molybdenum wire as the collector.

The starting point for the cell assembly was the sealing of the Nasicon disc on an α - Al_2O_3 tube using Kovar glass powder mixed with glycerine. After applying a thin paste of this mix to one end of the tube, the electrolyte material was placed in position and allowed to heat to about 700°C in a furnace so as to soften the glass. Then a very slow cooling rate avoided cracking of the sealed onto the α - Al_2O_3 tube by the glass. This technique was successful on most discs, but with some, considerable sealing problems were encountered possibly due to the nature of the material.

The filling with sodium was carried out in the glove-box in an atmosphere of ultra-high purity argon to prevent aerial oxidation of the sodium. The cells once filled were bolted securely to prevent any air leakages and placed in a block-type aluminium heater that was maintained at 350°C ± 8°C. To ensure full safety precautions against possible hazards with the cells, a Metal-x fire extinguisher was purchased.

A Galvanostatic method was used for charging and discharging the cells using a 60V - 3.5A Thompson and Associates Ministat. The cells were initially given forming cycles of charge and discharge every five minutes at 0.25Acm^{-2} to activate the electrolysis. Once activated, they were then cycled every half-hour at a constant current density of 0.5Acm^{-2} (the area varies slightly due to differing sample area), using an automatic current reverser. The voltage of each cell was recorded with respect to time, the cell was assumed to be no longer functioning once the voltage decreased to zero volts.

III RESULTS AND DISCUSSION

The results are presented in chornological order. A typical impedance plot at 300°C for GEL-MP 2.0) #19, 1175°C - 16 hrs is shown in Figure 4 and the corresponding variation of the ionic resistivity with temperature is shown in Figure 5. The data fit a straight line and was analysed using the equation:

$$\log (T/\rho) - \log A - Ea/2.303 \quad (1/T)$$

where A is the Arrhenius factor and ρ is the resistivity.

The resistivity and activation energy calculated from the slope of the above equation are shown in Table II, together with the thickness and area of each ceramic disc.

The resistivities and activation energies of three discs are not available since on polishing, the material was prone to flaking. Those which were measured had values that were comparable to Na-B/B"-Al_2O_3 and were of the order of about 12-13 Ω.cm except the GEL-MP discs which were slightly higher ($\simeq$ 20 Ω.cm). The activation energy of most discs were very good (11-18 $kJmol^{-1}$) except the Nasicon glass discs which had a range of 25-29 $kJmol^{-1}$.

As mentioned earlier, two disc (#C and #D of GEL-H1.5) had given considerable sealing problems onto an α-Al_2O_3 tube with Kovar glass. A dozen attempts resulted in weak seals. The break always appeared to be at the ceramic/ceramic rather than at the glass/ceramic joint. This was indicative of the fragile nature of the ceramic materials as well as the problems posed during polishing.

The voltage of each cell was recorded and as soon as the electrolyte had deteriorated, i.e., when the cell potential had reached a constant

value close to zero, the cells were dismantled. Each cell had different cycle life depending on the degradation of the ceramic material. Since the cells could not be opened at room temperature because of the solidified sodium in the cell, a special heating mantle was built that could be operated in the glove-box to melt the sodium. Considerable safety precautions were taken in this procedure due to the high risk of sodium fires. During the dismantling, a steady stream of ultra-high purity argon was passed through the glove-box. The first cell to be opened was that designated GEL-MP 2.0)#17, 1175^{o}C - 1 hr. The electrolyte from this cell had completely disintegrated into fine particles in the sodium melt on dismantling. The particles of the ceramic were so finely dispersed in the sodium that they could not be recovered. The residual sodium was poured into liquid paraffin and stored in the glove-box.

The electrolyte from the cell designated GEL-MP 2.0)#19, 1175^{o}C - 16 hrs was recovered as a whole disc but on cleaning the residual sodium from the surface, the disc began to crumble. The crumbled disc on exposure to air changed colour from a silvery appearance (surface sodium) to a dark brown. A photograph of the remains of this disc is shown in Figure 6.

The rest of the cells once deteriorated, were opened in the same way and each time small broken pieces of the electrolyte, reminiscent of GEL-MP 2.0)#19, could be observed. In all cases, the Nasicon material could not be recovered as a whole disc. This is not surprising since in the uncycled state, the electrolyte was fragile enough to get chipped at the edges without much effort.

The voltage-time characteristics of each cell are shown in Figure 7. It can be noted that degradation may have occurred as early as day 8 on sample GEL-MP 2.0)#17, 1 hr and day 12 on sample GEL-MP 2.0)#19.

The sample designated GEL-Hl.5)#D, 1300^{o}C - 16 hrs, which endured most of the work in the sealing stage, not surprisingly gave a much lower cycle life than

its counterpart GEL-H1.5)#C, 1300°C - 1 hr. (4-5 days as opposed to 7-8 days).

Those designated Nasicon Glass #5, 975°C - 1 hour and Nasicon Glass #11, 975°C - 16 hours deteriorated more or less at the same time, although the cycle life in both cases was considerably lower than the GEL-MP materials (3-5 days). One factor in favour of the GEL-MP material was that there was no sealing problem.

The rest of the cells did not fare any better. The cycle life was of the order of 4-7 days (Figure 8).

It is interesting to note that a B/B"-Al_2O_3 ceramic cell was also in operation at the same time as the Nasicon cells and at the time of opening this cell, it had a cycle life of about 80 days or about 2000 cycles. It is well worthwhile to illustrate the state of the disc after opening the cell as well as the voltage-time characteristics (Figures 9 and 10 respectively) in comparison with the Nasicon ceramics. The result speaks for itself.

CONCLUSION

It can be inferred from these results that none of the Nasicon material so far tested in cells is durable either in the uncycled or cycled state.

TABLE I

SAMPLE	SINTERING TEMP./°C	SINTERING TIME/hr	DENSITY/g.cm^{-3}
GEL-MP2.0)#19	1175	16	3.07
GEL-MP2.0)#17	1175	1	2.93
GEL-H1.5)#C	1300	1	3.27
GEL-H1.5)#D	1300	16	3.22
Nasicon Glass #5	975	1	
Nasicon Glass #11	975	16	
MP1.5(BM/SD)#27	1150	16	
MP1.5(BM/SD)#29	1150	1	
GEL-MP1.5(E)#C	1150	16	

TABLE II

SAMPLE	THICKNESS/mm	AREA/cm^2	RESISTIVITY@300°C/ .cm	ACTIVATION ENERGY/$kJmol^{-1}$
GEL-MP2.0)#17	2.25	5.208	21.8	16.47
GEL-MP2.0)#19	1.75	5.128	18.0	10.95
GEL-Hl.5)#C	2.98	5.108	11.8	13.62
GEL-Hl.5)#D	2.80	4.909	13.7	17.75
NASICON GLASS#5	4.24	4.301	13.2	25.6
NASICON GLASS#11	4.17	4.282	11.7	28.9
MPl.5(BM/SD)#27		3.140	Not Available	
MPl.5(BM/SD)#29		2.960	Not Available	
GEL-MPl.5(E)#C		2.550	Not Available	

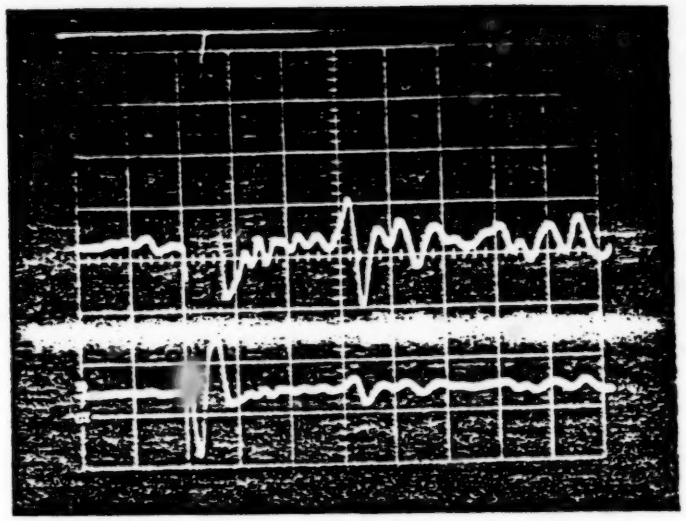
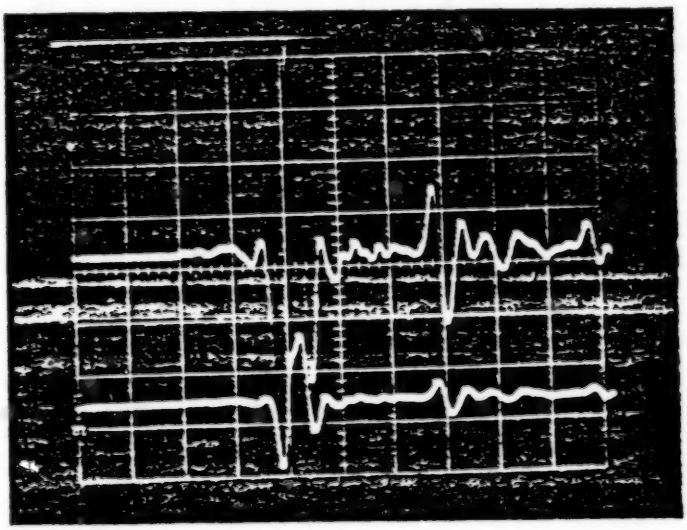

FORWARD REFLECTION
SCAN THROUGH SAMPLE
BACKWARD REFLECTION

FIGURE 1



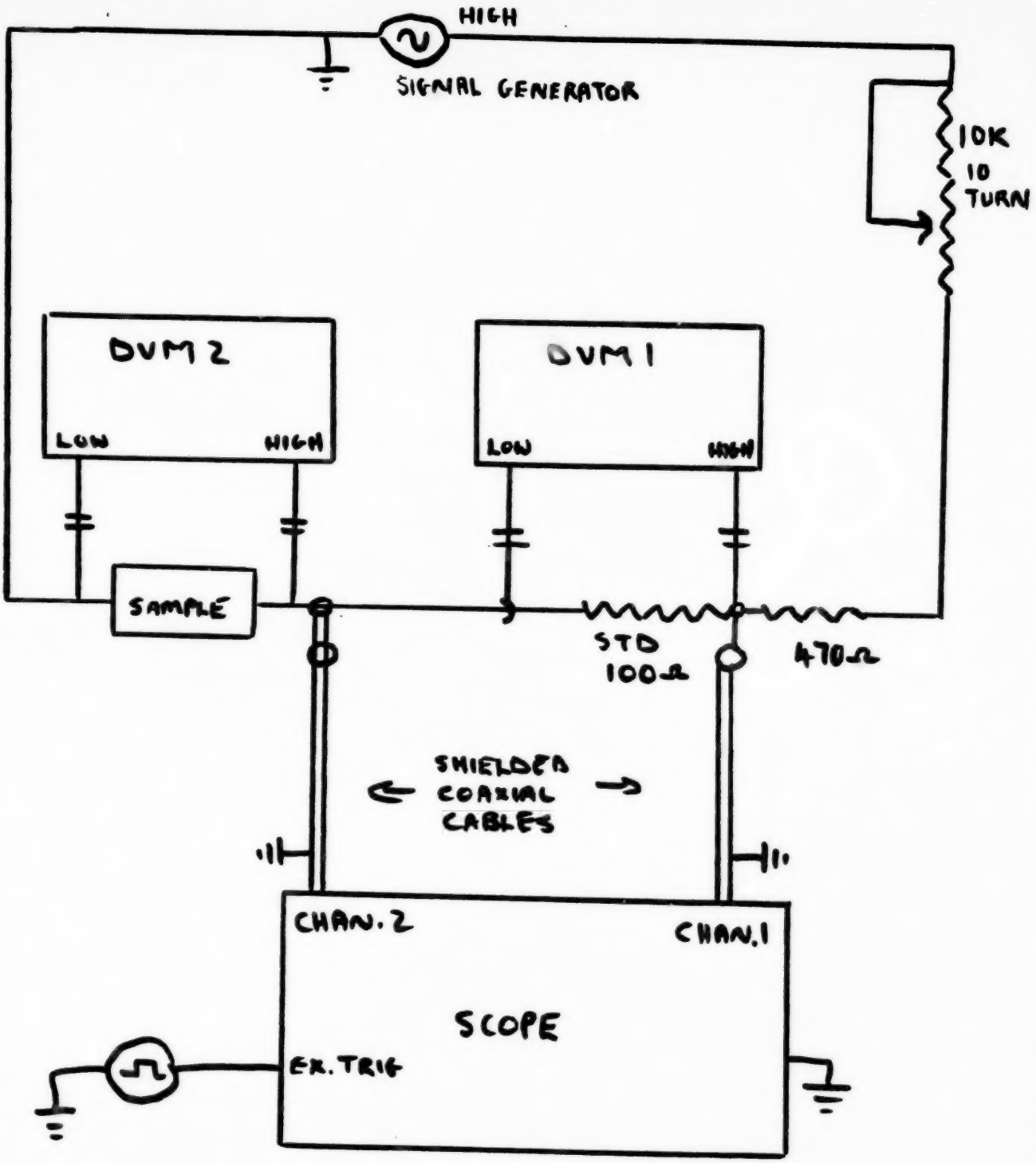

HIGH
SIGNAL GENERATOR
10K
10
TURN
DVM 2
LOW
HIGH
DVM 1
LOW
HIGH
SAMPLE
STD
100Ω
470Ω
SHIELDED
COAXIAL
CABLES
CHAN. 2
CHAN. 1
SCOPE
EX. TRIG

FIGURE 2.

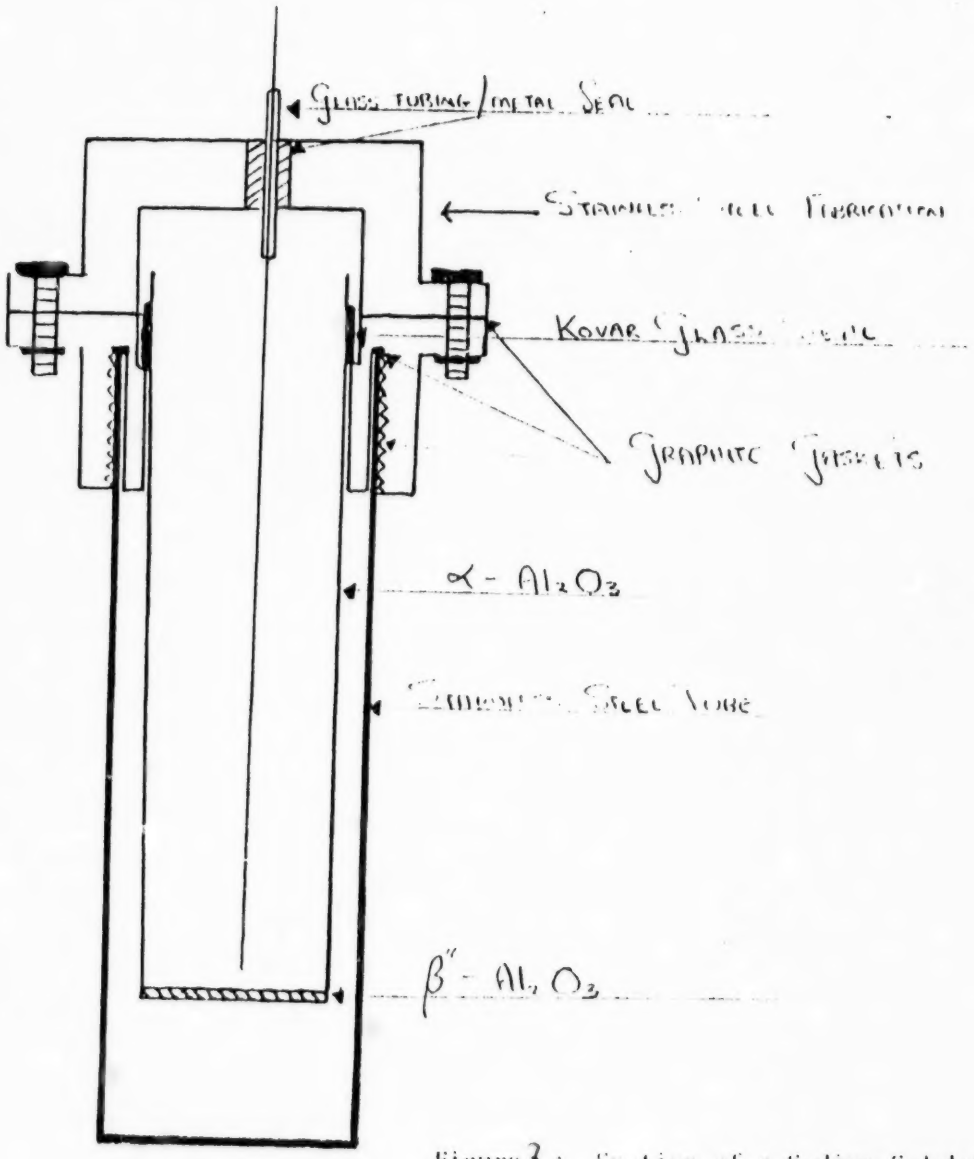


Figure 3 : Section of a Sodium-Sulphur Cell

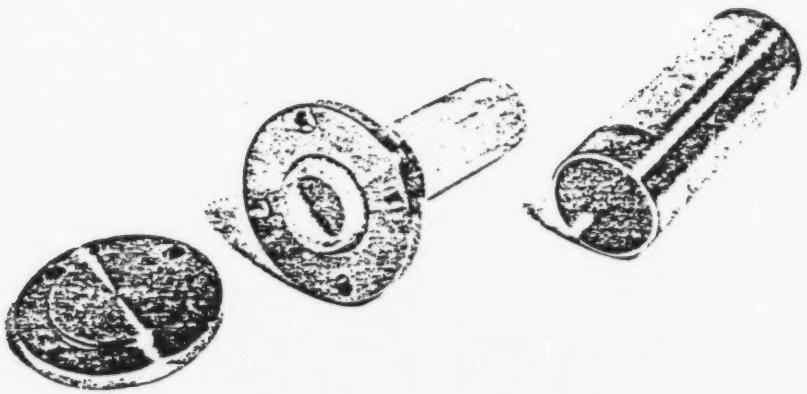


Figure 4

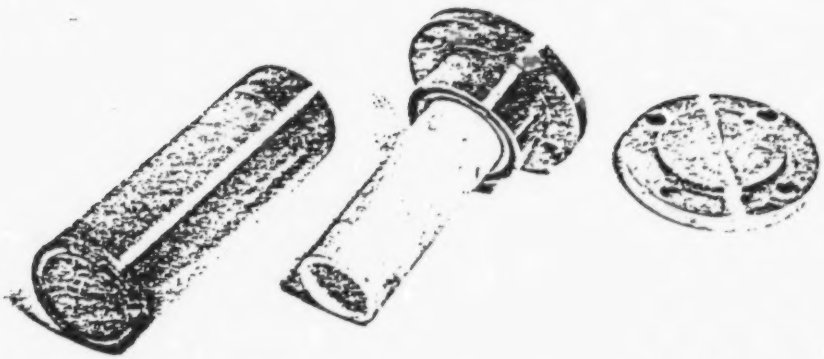


Figure 5

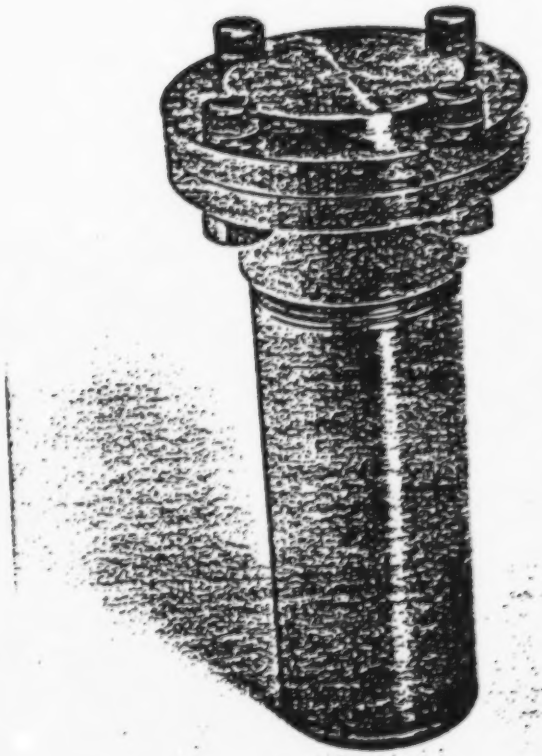


Figure C

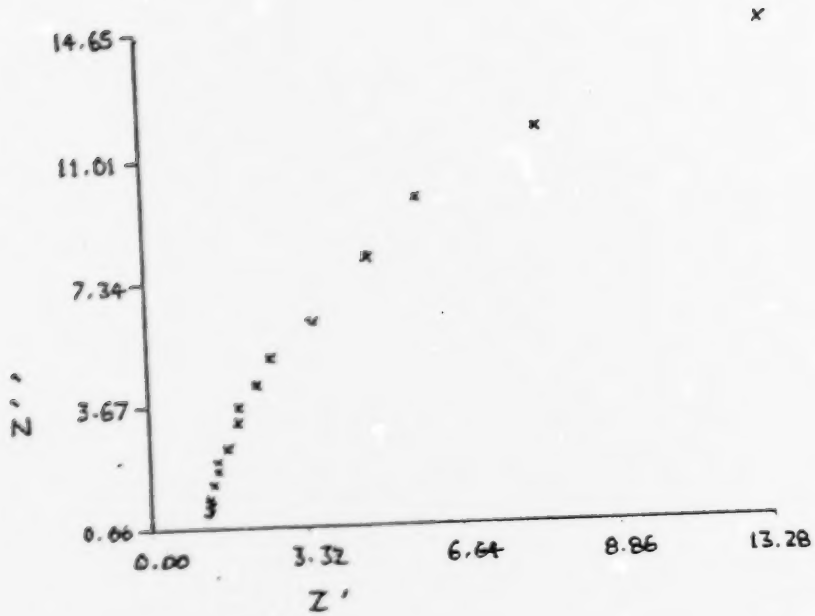


FIGURE 7.

Activation energy = 10948.0 J. Proportionality Constant (A) = 319.92087 K/ohm-cm

TEMPERATURE (K)	RESISTIVITY (ohm-cm)	D.C. RESISTANCE (ohms)	CROSS SECTIONAL AREA (cm2)	LENGTH (cm)
548.000	18.74	1.1180	2.9260	0.17
573.000	18.08	1.0787	2.9260	0.17
593.000	17.18	1.0249	2.9260	0.17
613.000	16.24	0.96920	2.9260	0.17

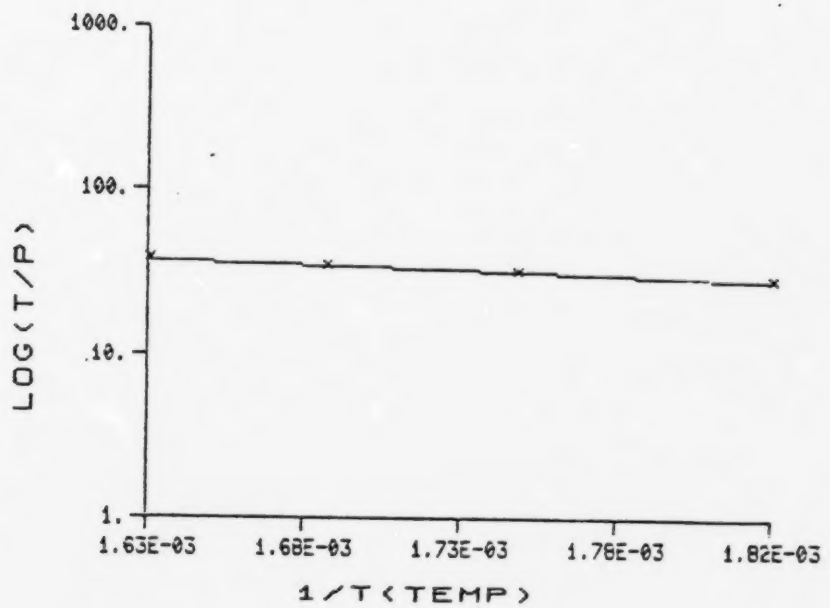


Figure 8

Figure 9A GEL MP 2.0)#19, 1175°C-16 hrs

Figure 9B β''-Al_2O_3 ceramic electrolyte

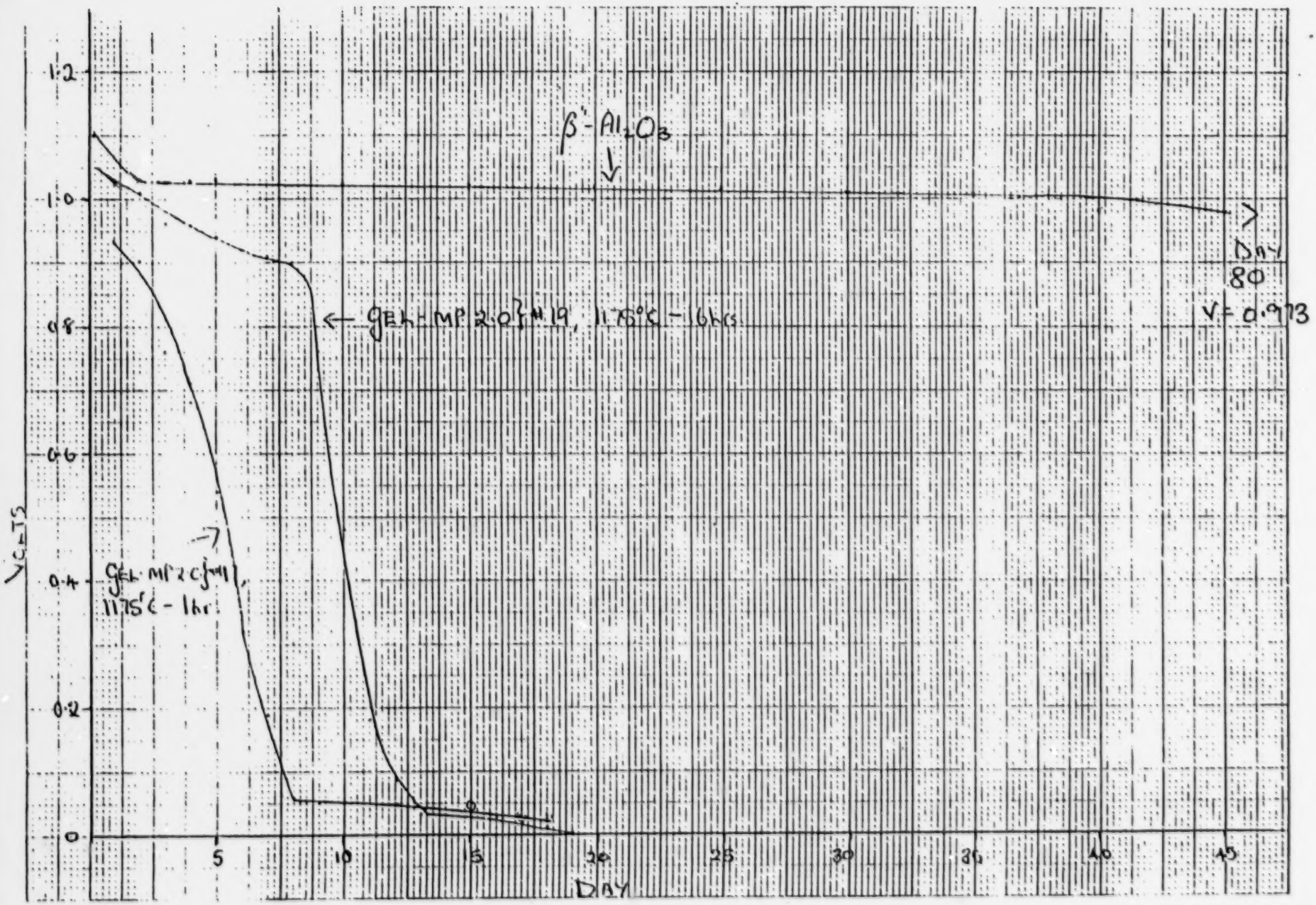

β'-Al2O3
← GEL-MP 2.0}H19, 1175°C - 6hrs
DAY 80
V = 0.973
GEL-MP 2 c}H1, 1175°C - 1hr
VOLTS
DAY
0
0.2
0.4
0.6
0.8
1.0
1.2
5
10
15
20
25
30
35
40
45

FIGURE 10

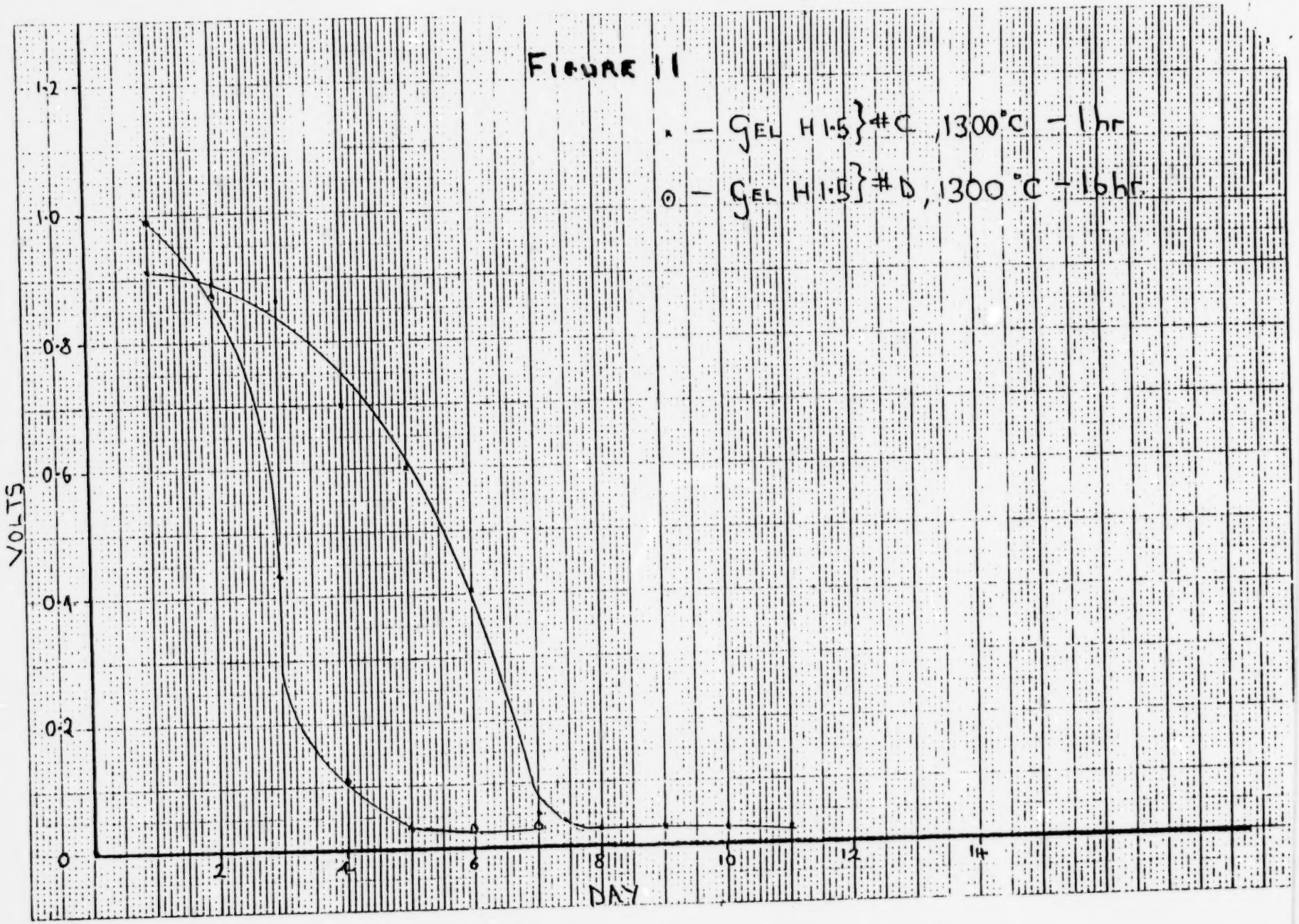


FIGURE 11
• — GEL H 1.5 } #C, 1300°C — 1hr
○ — GEL H 1.5 } #D, 1300°C — 16hr.
VOLTS
1.2
1.0
0.8
0.6
0.4
0.2
0
2
4
6
8
10
12
14
DAY

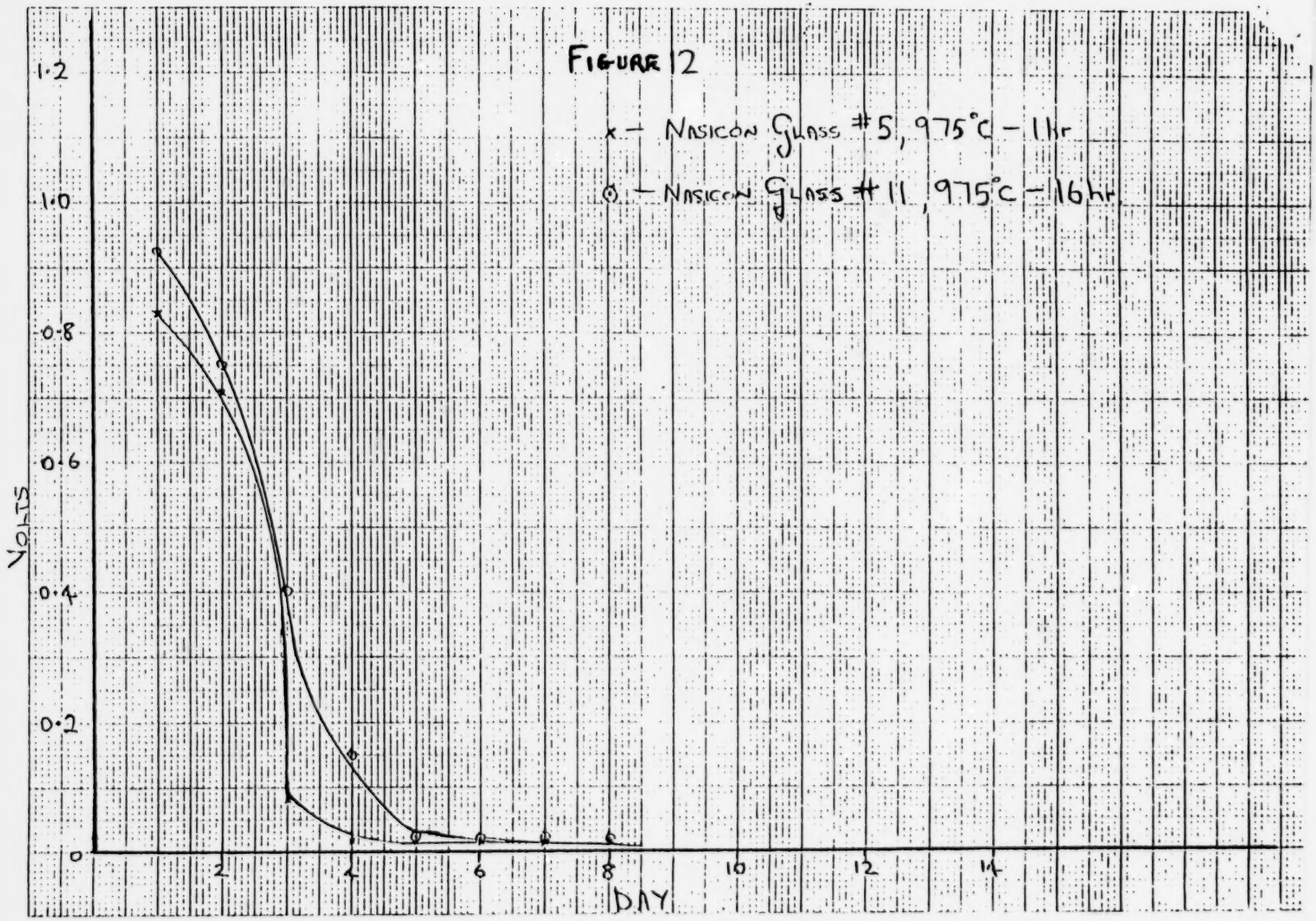


FIGURE 12
x — NASICON GLASS #5, 975°C – 1Hr
⊙ — NASICON GLASS #11, 975°C – 16Hr
VOLTS
1.2
1.0
0.8
0.6
0.4
0.2
0
2
4
6
8
10
12
14
DAY

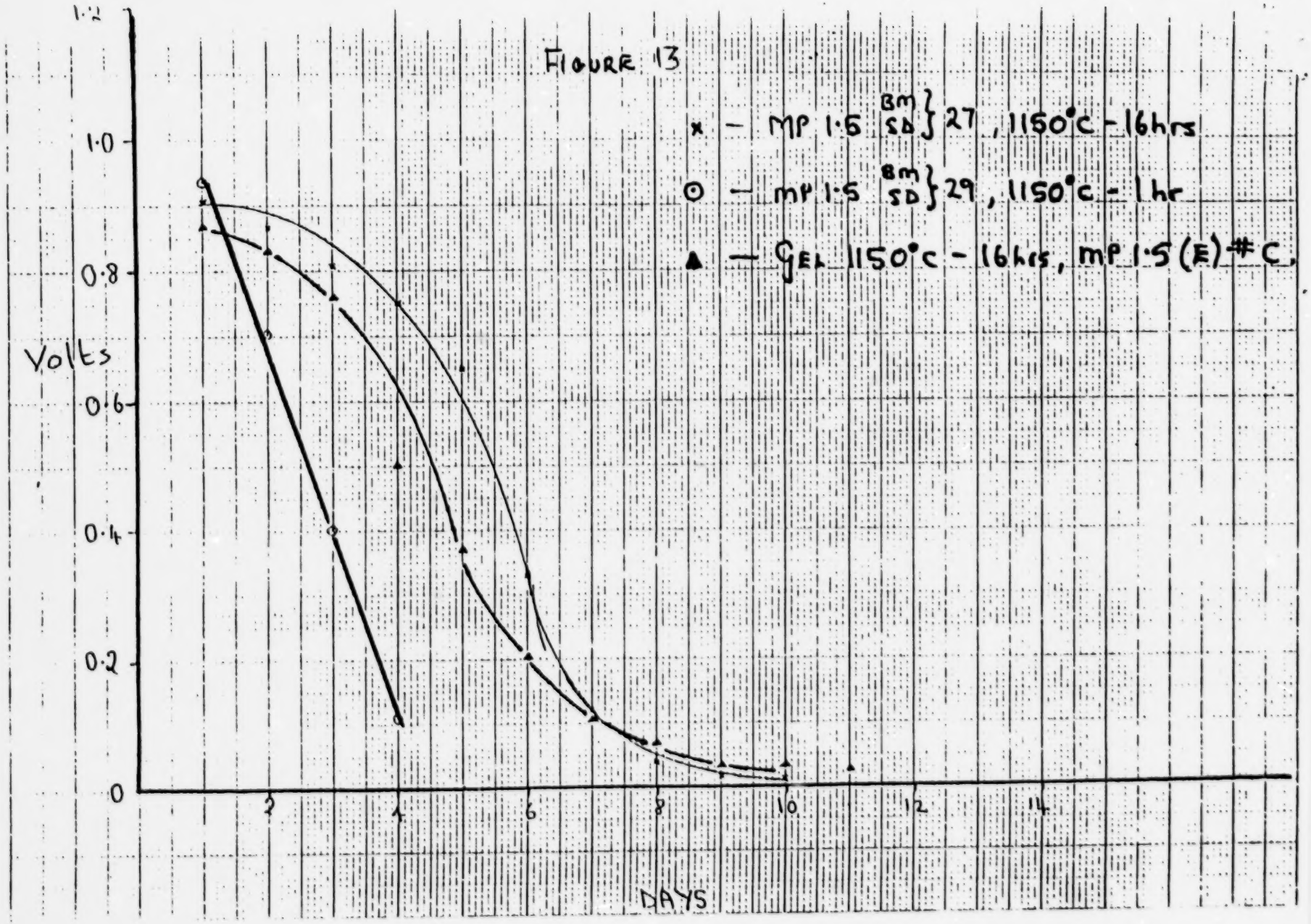


FIGURE 13
× — MP 1·5 BM SD } 27, 1150°C - 16hrs
⊙ — MP 1·5 BM SD } 29, 1150°C - 1hr
▲ — GEL 1150°C - 16hrs, MP 1·5 (E) #C,
Volts
1·2
1·0
0·8
0·6
0·4
0·2
0
2
4
6
8
10
12
14
DAYS

POOR

QUALITY

ORIGINAL